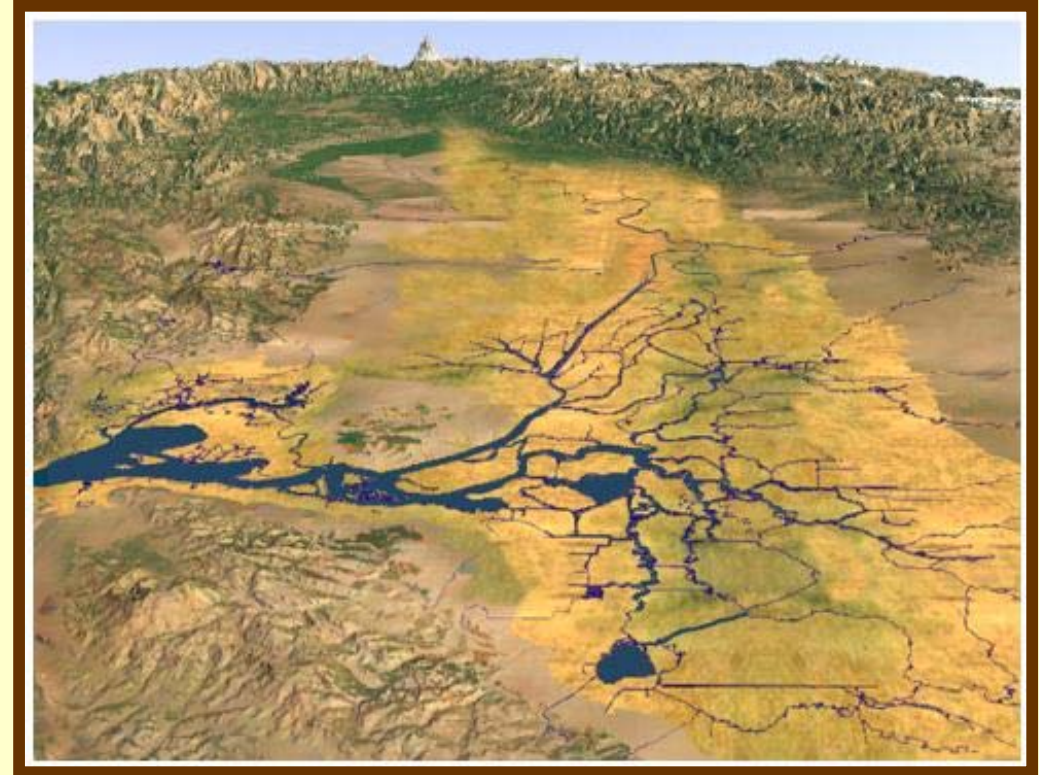


Workshop: The Development of a Research Framework To Assess the Role of Ammonia/Ammonium In the Sacramento-San Joaquin Delta and Suisun Bay Estuary Ecosystem

- **Introductory Remarks**
- **Chemistry of ammonia and ammonium**
- **Biogeochemical pathways for ammonium/ammonia**
- **Elemental stoichiometry**



Cliff Dahm
CALFED Lead Scientist



Workshop on the Impacts of Ammonia/Ammonium on the Delta

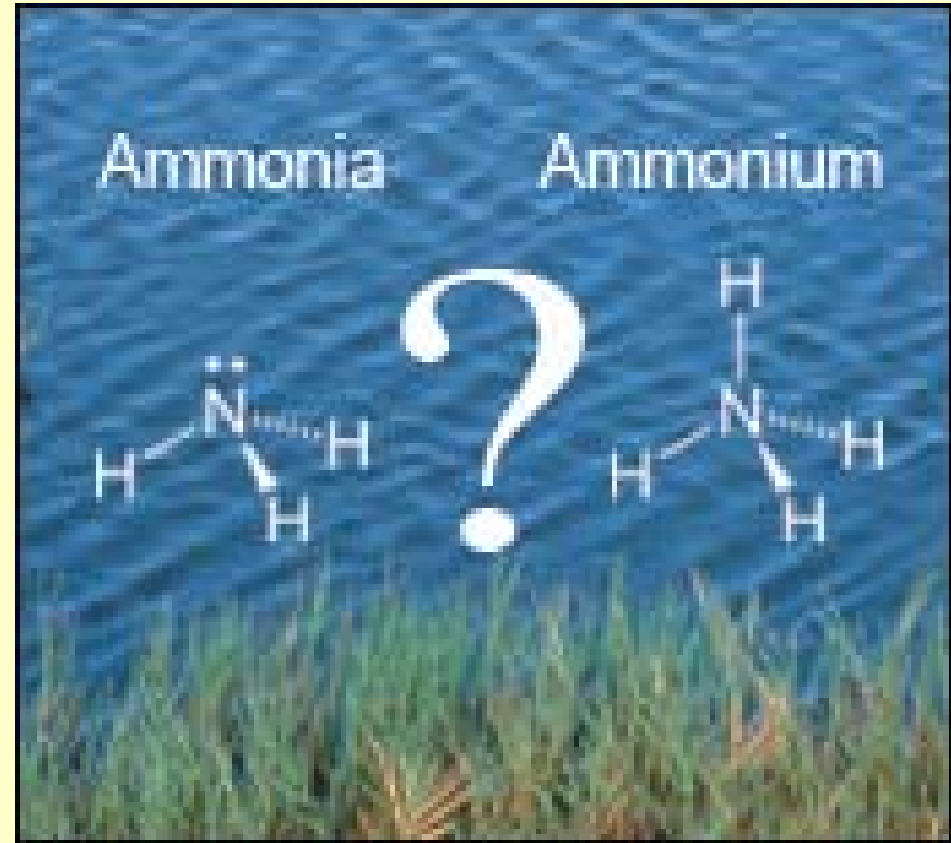
- Jointly funded workshop by the Sacramento Regional County Sanitation District (SRCSD) and the State Water Contractors (SWC)**
- Organizing Committee – Al Vargas (CALFED), Karen Larsen (CVRWB), Cameron Irvine (CH2M Hill), Frances Brewster (SCVWD), Rich Breuer (DWR), Adam Ballard (CVRWB)**
- Expert Panel – Amelia K. Ward (University of Alabama), Hans W. Paerl (University of North Carolina), Patrick J. Mulholland (Oak Ridge National Laboratory), and Joseph S. Meyer (University of Wyoming – emeritus)**

Primary Goal for the Workshop

- **Develop a research framework for the study of ammonia and ammonium in the Delta and Suisun Bay**
- **Research Framework – a vision for the future of scientific investigation**
- **Examples: National Science Foundation, National Academy of Sciences, and the European Union**
- **Drawn from the expertise of external panelists, local experts, and key stakeholders**
- **CALFED Science Program – our mission is science coordination, integration, stimulation and communication**

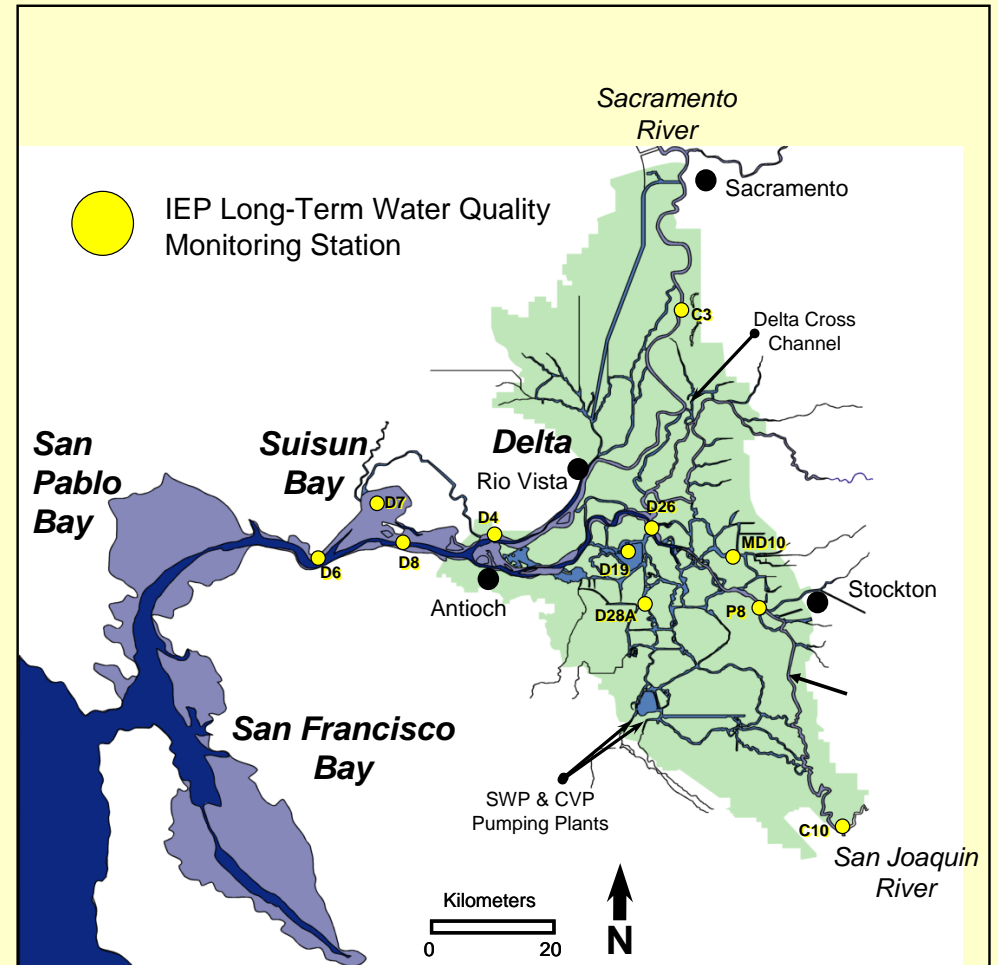
Chemistry of $\text{NH}_3/\text{NH}_4^+$

- Ammonium (NH_4^+) – positively charged ion; easily measured
- Ammonia (NH_3) – un-ionized gaseous form; difficult to measure
- Equilibrium reaction
$$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$$
- $\text{pH} = -\log [\text{H}^+]$
- Total Ammonia =
$$(\text{NH}_3) + (\text{NH}_4^+)$$



Chemistry of $\text{NH}_3/\text{NH}_4^+$

- 50/50 mixtures of ammonia and ammonium at pH 9.73 at 10°C, at pH 9.40 at 20°C, and at 9.09 at 30°C
- 10/90 mixtures of ammonia and ammonium at pH 8.73 at 10°C, at pH 8.40 at 20°C, and at 8.09 at 30°C
- 1/99 mixtures of ammonia and ammonium pH 7.73 at 10°C, at pH 7.40 at 20°C, and at 7.09 at 30°C
- Increasing salinities decrease ammonia concentrations



Chemistry of $\text{NH}_3/\text{NH}_4^+$

Example Calculation: How much un-ionized ammonia (NH_3) is present in a freshwater sample with 1.0 mg/L ammonium ($\text{NH}_4^+\text{-N}$) and an in situ pH of 8.0 and a temperature of 20°C?



$$K = \frac{[\text{NH}_3] * [\text{H}^+]}{[\text{NH}_4^+]}$$

pH = $-\log [\text{H}^+]$; $[\text{H}^+] = 1 \times 10^{-8}$; pK = 9.40; $K = 3.98 \times 10^{-10}$

$\text{NH}_4^+\text{-N} = 1.0 \text{ mg/L} = 1000 \text{ } \mu\text{g/L} = 71.43 \text{ } \mu\text{M} = 7.143 \times 10^{-5} \text{ M}$;

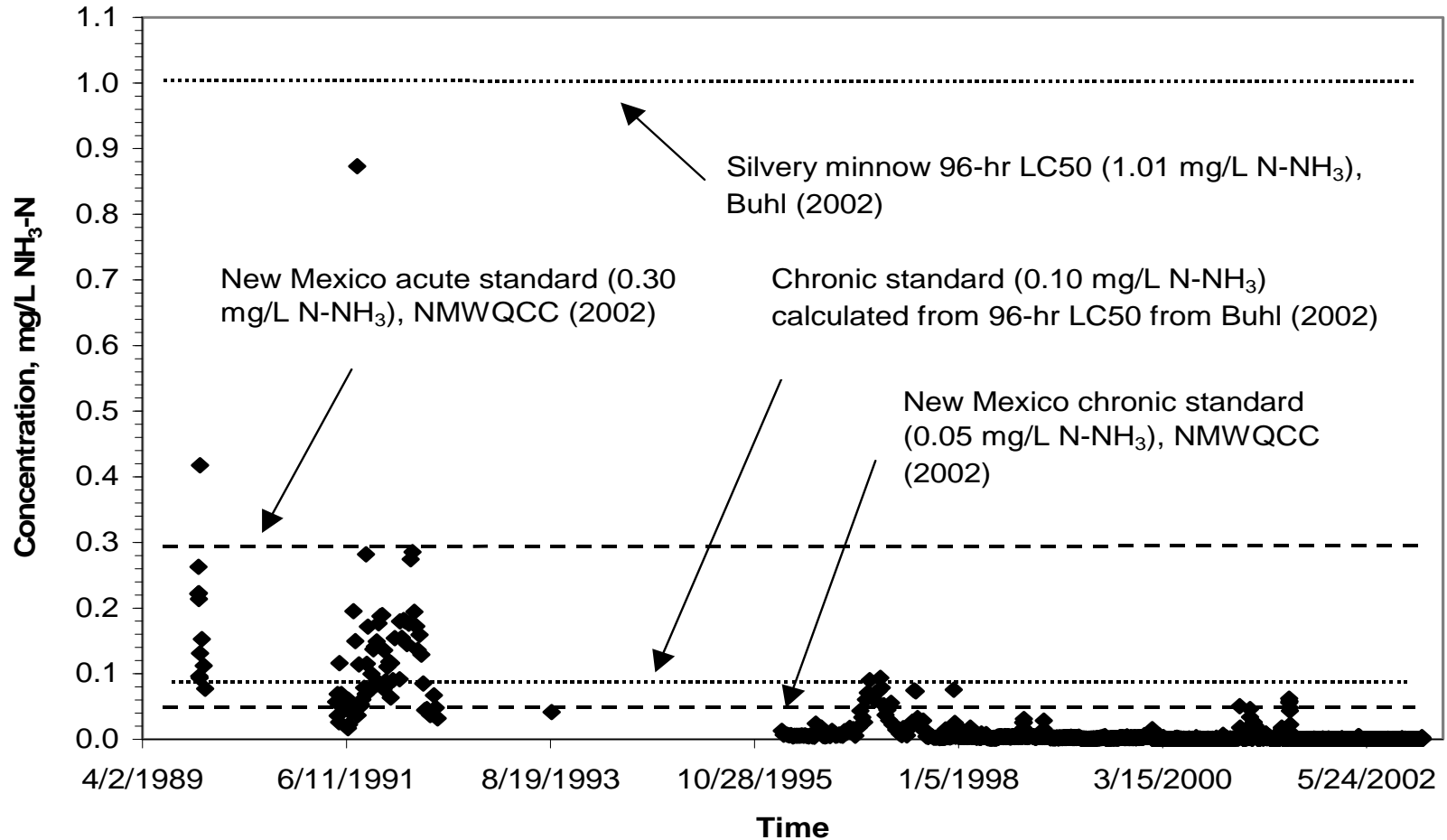
Convert from $\text{NH}_4^+\text{-N}$ to $\text{NH}_4^+ = 9.18 \times 10^{-5} \text{ M}$

Solving for $[\text{NH}_3] = 3.65 \times 10^{-6} \text{ M}$ or $62 \text{ } \mu\text{g/L}$ or $.062 \text{ mg/L}$

Higher pH values increase un-ionized ammonia concentrations, higher temperatures increase un-ionized ammonia concentrations, and higher salinities decrease un-ionized ammonia concentrations (Emerson et al. 1975)

Model results: NH_3 (un-ionized ammonia) concentrations averaged from 60 model runs

From Passell et al. (2007) Ecological Applications



Average daily NH_3 -N concentration, 1989-2002, from 60 runs of the model. New Mexico standards are for warm water fisheries at pH 8.0 and 25 degrees C.

NITROGEN CYCLE

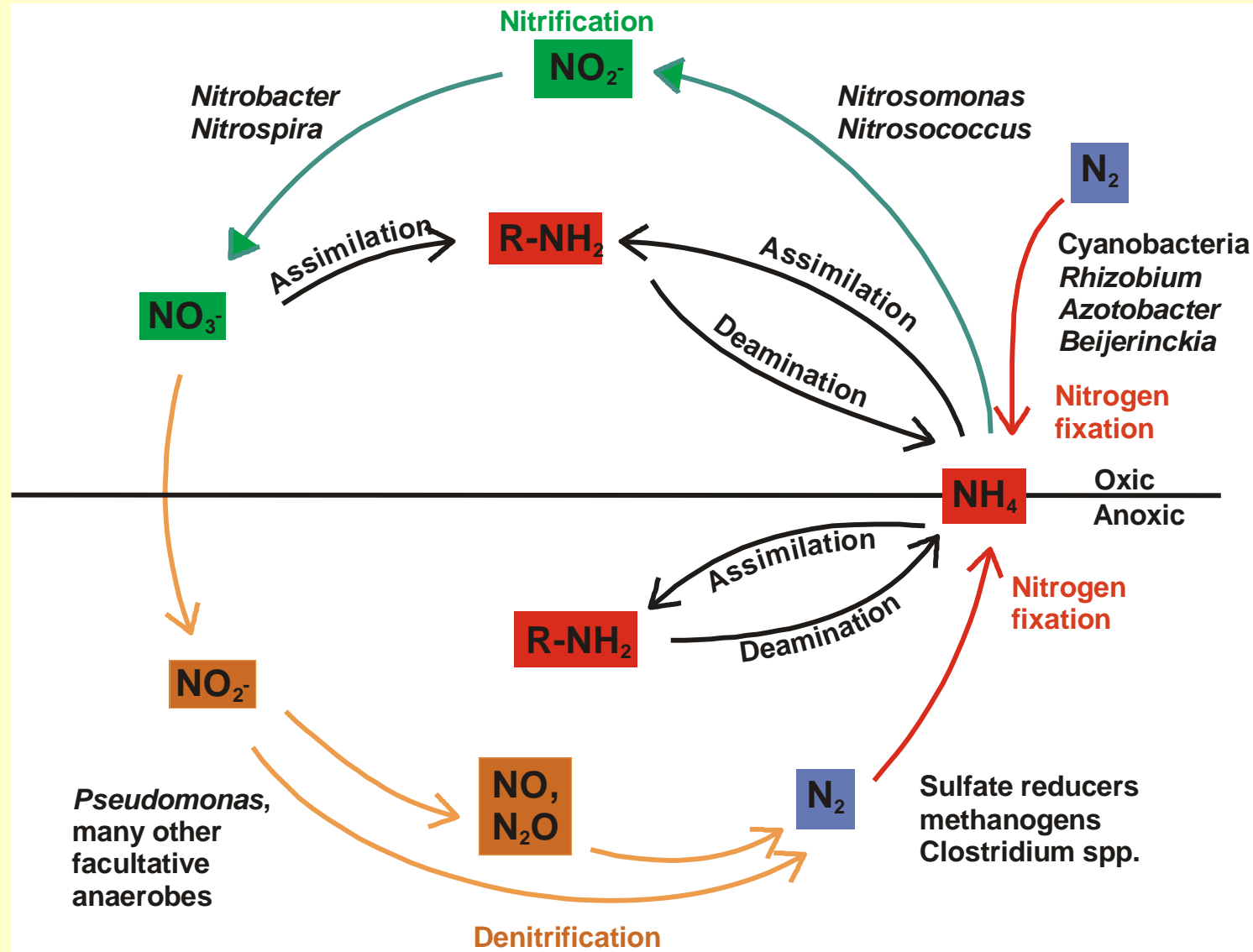
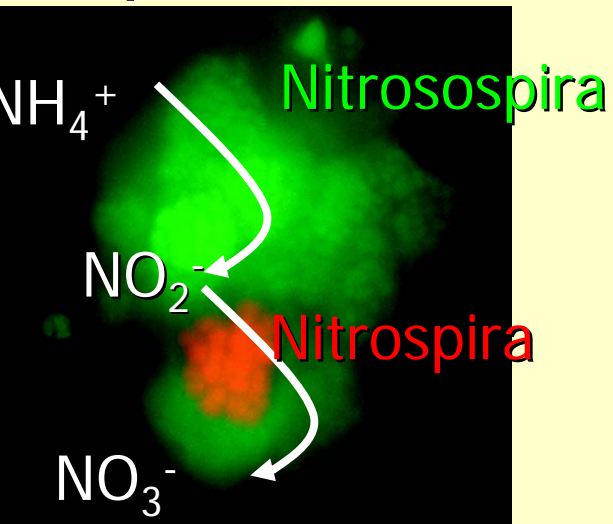
World oceans and freshwaters

Terrestrial systems

Agriculture

Waste water

Aquaria

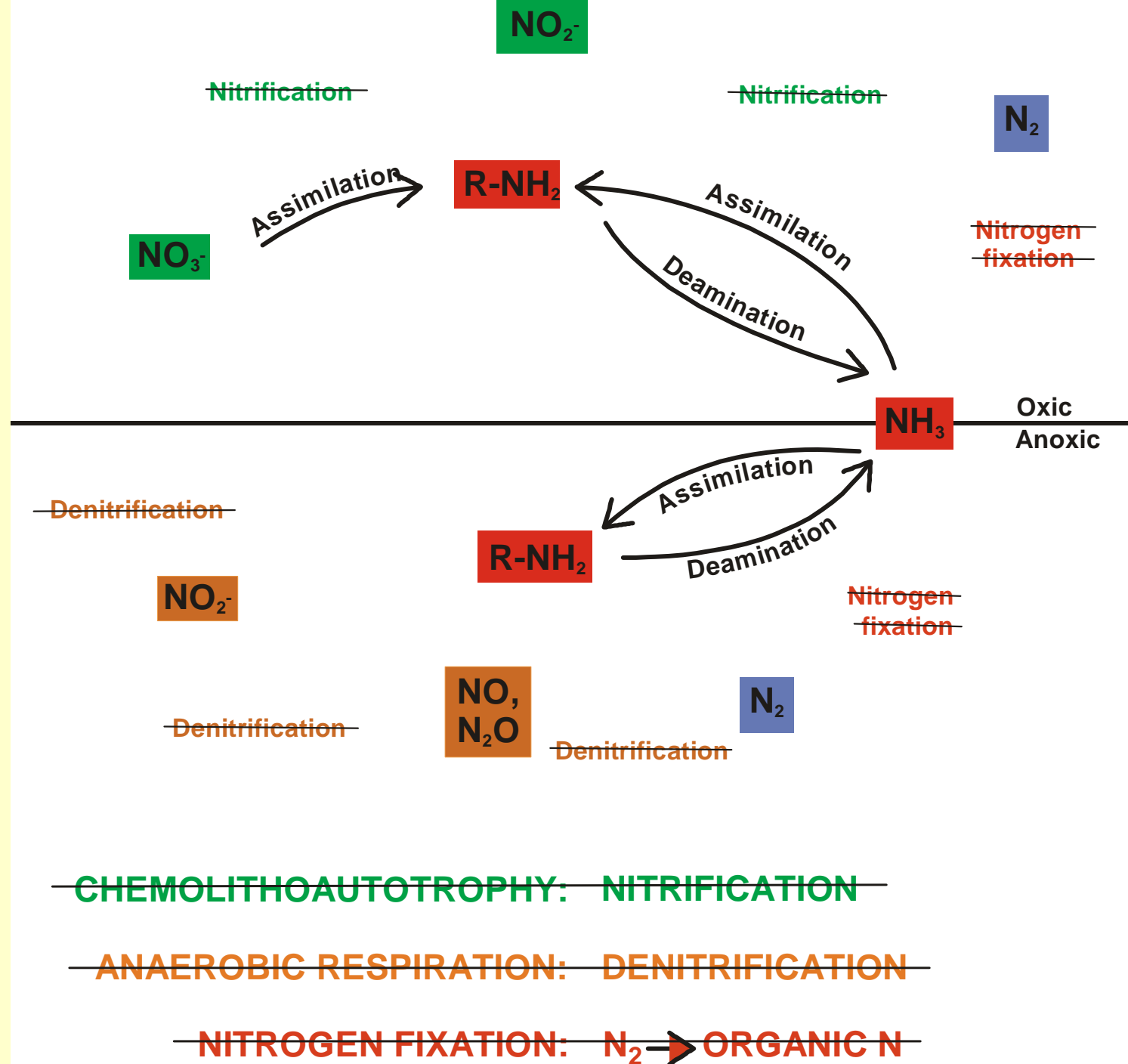


CHEMOLITHOAUTOTROPHY: NITRIFICATION

ANAEROBIC RESPIRATION: DENITRIFICATION

NITROGEN FIXATION: $\text{N}_2 \rightarrow$ ORGANIC N

NITROGEN CYCLE (MINUS MICROBES)



Elemental Stoichiometry

- “Improvements in the water quality of many freshwater and most coastal marine ecosystems requires reductions in both nitrogen and phosphorus inputs”
Conley et al. (2009) *Science* 323:1014-1015
- Redfield Ratio:
106C:23Si:16N:1P
- Do not consider ammonium independently from other nutrients in the ecosystem

